Bull. Environ. Contam. Toxicol. (1998) 61:477-483

Bulletin of Environmental Contamination and Toxicology

Diazinon Residues in the Basins of Anzali Lagoon, Iran

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Received: 14 June 1998/Accepted: 31 August 1998

The Anzali lagoon is an internationally important wildlife reserve and wintering area for water-fowl. It also serves as an important spawning and nursery ground for the economically important anadromous fish. Another function of this freshwater coastal lake is that it traps sediments from the watershed of many streams and about fifteen rivers(Keudler 1978; Olah 1990).

Diazinon is the most widely used pesticide of the recefields in the Anzali basin watershed. This insecticide has been used as 5% and 10% granule to control rice stem borer (*Chilo suppressalis*) since 1974. Following granule application in rice paddy fields, the insecticide is released into water and enters streams which serve as the drainage of the ricefields. The streams and rivers finally discharge the pesticide load into the lagoon. The mobility of diazinon has been reported by Readman et al.(1992) and Larson et al.(1995).

Several cases of fish mortality in the lagoon have been occurred during recent years. Pesticide pollution was suspected to be the main reason for the death of different species of fish (*Cyprinus carpio, Carassius auratus, Esox lucius, Perca fluviatilis*) in November 1991, June 1993 and July 1996.

In the present study the level of diazinon was investigated in the surface water and sediment of the lagoon. The study began in May 1996 and continued until February 1997. In order to elucidate the pattern of diazinon pollution in the streams and rivers, one effluent river from central basin of the lagoon was chosen and the water samples were analyzed for the residue during the granule application season in ricefields.

MATERIALS AND METHODS

Diazinon standard of 99% purity was obtain from Nichimen Company, Minato, Tokyo, Japan. All solvents (acetone, haxane and diethyl ether) and other chemicals used for extraction, clean-up and other purposes were of analytical grade.

Three permanent sampling stations were established along the Anzali lagoon. These stations were located in the eastern, central and western basins of the Anzali lagoon (figure 1). The sampling usually occurred from 15th to 20th of each month.

Duplicate water samples from the surface were collected in 1000 ml glass bottles by boat and extracted upon arrival at a local station. Sediments were sampled using a grip. The

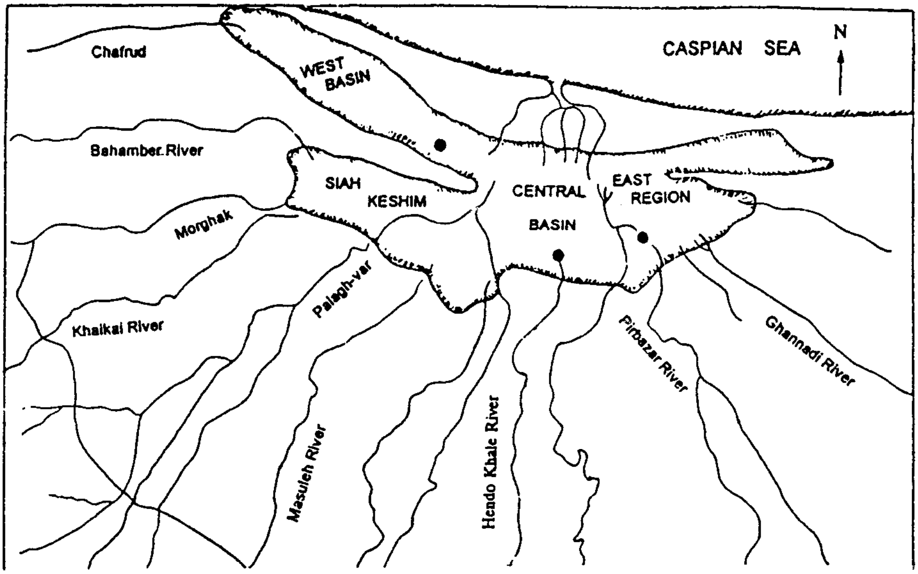

Figure 1. sampling stations (●) for diazinon residue assessment in Anzali lagoon

grip was thrown into the sediment at a depth of 5-10 cm in the bottom of the lagoon and then was pulled out. At least two sediment samples (1000 g) were collected from two places at each station and transferred into plastic bags and stored at approx. -10° C until analyzed not more than 48 hours later. No alteration in residues occurred in samples by aeration, filtration or additional procedures prior to analysis. Results of the analysis of the sediment samples are summarized in Table 1.

Table 1. Characteristics of the three experimental station sediments along the lagoon.

Place of sampling	Texture			%OM	pH	Class
	%clay	%silt	%sand			
East	37.6	37.6	24.2	5.4	7.3	Clay loam
Central	21.6	49.6	28.8	3.5	7.5	Silty loam
West	19.5	47.6	32.8	9.3	7.5	Siltv loam

Water samples without any filtration were extracted according to the procedure described by Zweig and Devine(1969). The method can be summarized as follow:
1000 ml water was placed in a 2 litre separatory funnel. Ten ml saturated aqueous sodium chloride solution was added and the sample extracted successively with 100, 50 and 50 ml hexane. The hexane combined extracts was passed through 40 g anhydrous sodium sulfate and then evaporated to 2-3 ml. This solution was placed in 10 ml stoppered tube and left in a refrigerator for further analysis.

After bringing the samples into the laboratory on ice, the extract was evaporated to dryness under nitrogen current and the residue redissolved in 50 µl of acetone. Twenty µl of this solution was spotted on chromatoplate (Plastic sheet coated with silica gel 60 F_{254}), along with standard diazinon. The plate was developed in diethyl ether+hexane (75:25 by volume) for a distance of 15 cm and after drying the related spots were inspected under U.V. light. The silicagel areas opposite to the related standard compounds were cut and eluted with 2-4 ml acetone. After evaporation of acetone, the residue was redissolved in a small volume of acetone. This final solution was used for injection into the G.C. system.

Sediment samples were analyzed using the method of Sethunathan et al.(1971). Fifty g of sediment sample with known moisture was placed in a bottle with 50 ml acetone and shaken for 30 minutes, then 50 ml hexane and 25 g anhydrous sodium sulfate was added and shaken for another 30 minutes. The mixture was allowed to stand overnight. Twenty five ml of supernatant was taken by pipette and evaporated to 2 ml by a rotary evaporator. This extract was then cleaned-up according to the above-mentioned procedure for water sample.

The G.L.C. was a Varian Aerograph series 2700, fitted with AFID detector. The gas chromatograghic operating conditions were: column: stainless steel (2-mx3-mm I.D.) packed with 5% SE-30 on chromosorb WHP (80-100 mesh). Flow rate of nitrogen was 17 ml/min. Temperature were: column 180°C injection port 210°C and detector 205°C.

Recovery experiments were conducted with water and sediment samples from central station and compared with similar samples without fortification. The water samples fortified at the level of 0.1 and 0.5 mg/L. Each fortification level was prepared in two replicates, Recoveries observed for these two levels were 92.3% and 89.1% respectively. The recoveries of diazinon from sediments samples fortified at 0.04 and 0.08 µg/g were 90.5% and 85.2% respectively.

RESULTS AND DISCUSSION

The concentration of diazinon in water samples from Hendo Khale river was shown in figure 2 at 15 days intervals from 15 June to 15 September 1996. Diazinon levels detected in the river water were high during June and July, reaching a concentration in water at 200 to 270 ng/L. The residue declined by the August and reached a constant level by the end of August and September. The lowest concentration of diazinon found in September was 62 ng/L.

The pattern of diazinon residue in water samples from lagoon is shown in figure 3. In May 1996, the residue found in three stations were different, with the lowest level in central and the highest level in the western station. These level increased in the next month and again the west station showed the highest residue level. The maximum diazinon concentration found in this study was 380 ng/L in July 1996 in the east station. From August, the residue declined rapidly to very low levels. During October and November a slight variation was detected in the diazinon residue. An increase in the residue concentration was observed in the water samples of some stations in the last month of 1996, but the level of residue was not as high as those found in the late spring and the early summer. A decline in residue level started in January 1997 and the lowest level of residue (4-11 ng/L)) in this study was found in February 1997.

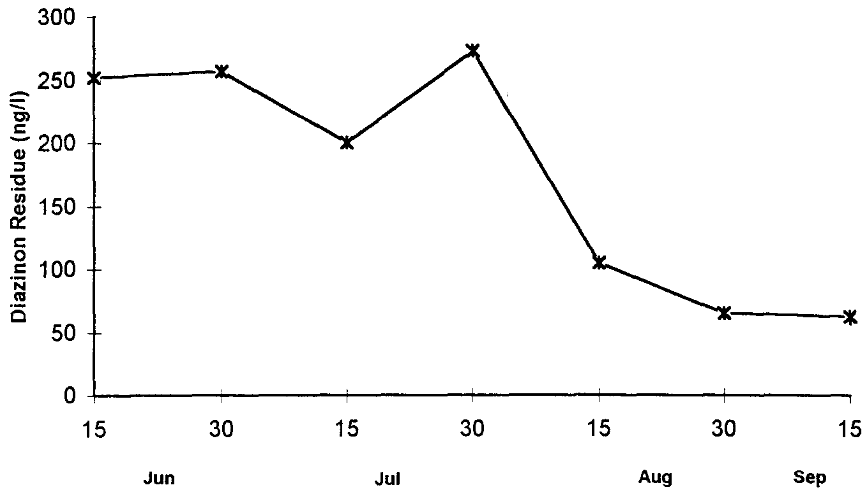

Figure 2. Diazinon residue in the surface water of one of influent river (Hendo Khale) during granule application period (15 June to 15 September 1996).

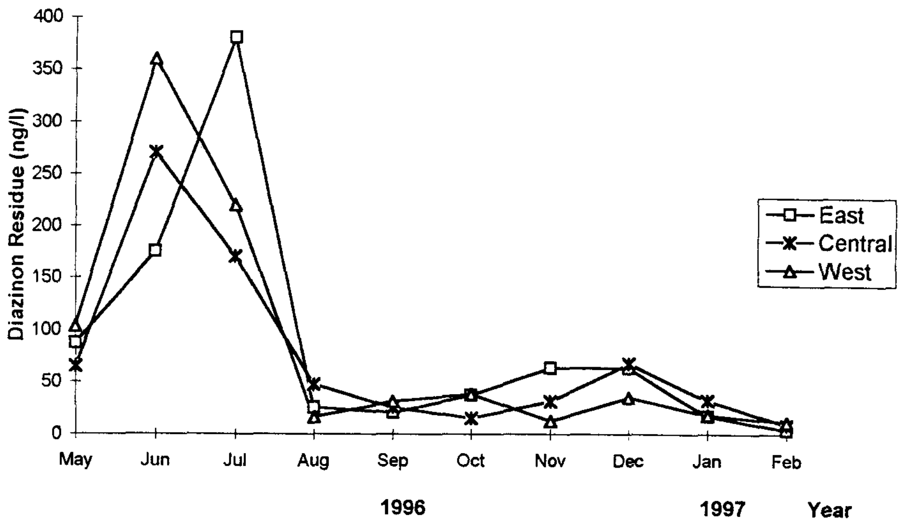

Figure 3. Residue of diazinon found in water samples collected from three stations in Anzali lagoon.

During the first two months of this study an increase in residue level was observed in the sediments of all sampling stations.(figure 4). This increase was mainly in eastern and western stations. A decline in residue concentration started from July and continued in August. The minimum level of residue was recorded in September and less than 1 ng/g diazinon was recovered from the sediments in eastern and central stations. From October

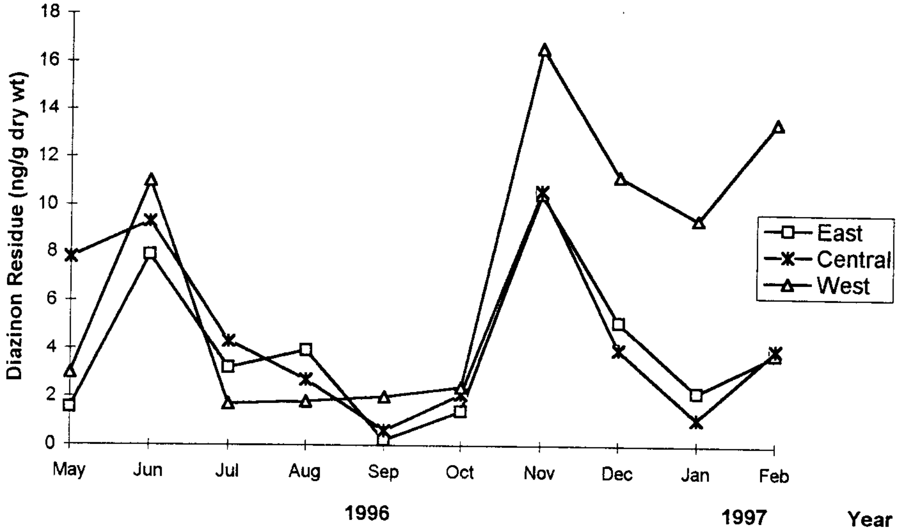

Figure 4. Residue of diazinon found in sediment samples from three stations in Anzali lagoon.

an increase in diazinon residue was observed and the largest amount was obtained in November in western station. This was about 17 ng/g which declined thereafter. A rapid decline in insecticide concentration was observed in eastern and central stations from December, but in the western station the rate of decrease was much slower than the other stations in December 1997. In February, the samples from western station had shown a high residue level which was three times greater than residue from other stations.

The residue concentration of diazinon in Hendo Khale river was a function of the time of application of this insecticide in ricefields. The longer the time interval between application of insecticide in fields and sampling of the water in the river, the lower residue concentration was found.

Levels in surface water of the lagoon showed more or less the same trend as in the water of the river during the year. The first residue peak in water occurred in June and July which is highly significant. This maximum coincide with diazinon application in the ricefields. The residue dropped off sharply from August to a very low level. Following its release in the water diazinon was gradually declined due to hydrolysis, volatilization, photolysis, and high temperature (>25°C). These factors may accelerate the removal of chemicals from water during the summer months, in addition to the influent water that reaching the lowest level during this period. The transportation of residue by water into the Caspian Sea in summer is less probable, since water level in the lagoon could decline to such an extent that Caspian Sea water is washed into the lagoon, although the lagoon is three to four meters in elevation higher than the Caspian Sea. The second peak which occurred during December is less easy to explain, however this maximum did coincide with the high rain. The correlation between residue and rainfall in this study is in agreement with the work of Harris and Miles(1975) who reported the dependence of residues of DDT in the water of

Upper Big creek and rainfall. According to Domagalski et al.(1997) diazinon concentration in the streams of San Joaquin River in California peaked within hours of the rainfall.

The residues of diazinon in sediments of the lagoon showed two peaks in June and November. Application of diazinon granule in paddy fields usually occurs mainly during the end of the May and early June. A few days after diazinon application, the paddy water carries the insecticide dissolved and bound to suspended solids and enter streams and tributaries which finally transported by the rivers into the lagoon. As a result of these incoming residues an increase in diazinon concentration took place. This coincide with the high residue level in water which reached a maximum level during June and July.

The second peak of residue in sediments occurred in November. The main reason for this increase in recovered diazinon is runoff. More than 50% of the annual precipitation in the lagoon watershed occurs during the autumn(Keudler, 1978), which may result in heavy flooding of the lagoon and transportation of particle bound diazinon into it. This flooding result in sedimentation of residue rich precipitation during this season.

Many factors are involved in the differences of the residue level among the samples of various stations. Usually the sediment load, organic matter, pH and temperature may affect the residue concentration. Meanwhile a remarkable point is the presence of higher residue level in the sediments of western station during November toward the end of the experimental period. The flow rate of water in this basin is lower than the other parts of lagoon and this allows a better precipitation of highly rich residue content sediments, beside the sediments of this station has higher organic matter percentage which has the capacity to absorb more pesticide than the other components of the soil. Diazinon is known to persist for extended period in organic soil(Miles et al., 1978).

These studies have shown that the concentration of diazinon reached even high level of contamination(up to 16.8 ng/g in sediment and 380 ng/L in surface water). Yet the possible adverse effects of diazinon residues observed on fish and other aquatic organisms of the Anzali lagoon is a question that requires further investigation.

Acknowledgments. This project was supported by the Iranian Department of the Environment, Guilan Province.

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